U.S. DEPARTMENT OF COMMERCE
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PB-270 979

Prototype Correlation Mask Flame Photometric Detector for Measuring Sulfur Dioxide

Baird-Atomic, Inc, Bedford, Mass

Prepared for

Environmental Sciences Research Lab, Research Triangle Park, N C

Jul 77

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-77-130	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE: PROTOTYPE CORRELATION MASK FLAME PHOTOMETRIC DETECTOR FOR MEASURING SULFUR DIOXIDE	5. REPORT DATE: June 1977
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): Author Hornig	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Baird-Atomic, Inc. 125 Middlesex Turnpike Bedford, Massachusetts 01730	10. PROGRAM ELEMENT NO. 1AA010 26AAP (FY-74)
	11. CONTRACT/GRANT NO. 68-02-0275
12. SPONSORING AGENCY NAME AND ADDRESS: Environmental Sciences Research Laboratory -RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED: Final
	14. SPONSORING AGENCY CODE: EPA/600/03
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution		13B
* Sulfur dioxide		07B
* Instruments		14B
* Flame photometry		20F
* Optical equipment		

18. DISTRIBUTION STATEMENT: RELEASE TO PUBLIC	19. SECURITY CLASS (This Report): UNCLASSIFIED	21. NO. OF PAGES: 42
	20. SECURITY CLASS (This page): UNCLASSIFIED	22. PRICE: NTIS $3.00

EPA Form 2220-1 (9-73)

PB 270 979

EPA-600/2-77-150
July 1977

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EPA-600/2-77-130
JULY 1977

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ABSTRACT

A prototype flame photometric detector system (FPD) to measure gaseous sulfur compounds was fabricated utilizing a previously developed correlation mask optical system and a new flame housing. Also, a new burner for the FPD system was optimized to view the excited molecular sulfur emission. The sample/hydrogen intake system was also redesigned to operate under a positive pressure, resulting in improved flame stability. The prototype detector system was equipped with a cooled photomultiplier with special optics to enhance sensitivity. Initial tests with the completed system indicated the capability of measuring sulfur dioxide at the part-per-billion level. Because of subsequent problems, an absolute calibration of the system was not carried out.

This report was submitted in fulfillment of Contract No. 68-02-0275 by Baird-Atomic, Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from 1972 to 1975, and work was completed as of July, 1975.

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SECTION 1

INTRODUCTION

The prototype flame photometric detector (FPD) for measuring sulfur dioxide, described in this final report, was developed as a logical sequel to earlier work (under Contract EHSD 71-30) on improving the optical efficiency of luminescence of an existing FPD. A new flame housing was designed, fabricated, coupled to the previously developed optics, and tested. The new burner was optimized to view the excited sulfur emission (S_2^*) with the previously developed correlation mask. The sample/hydrogen intake system was also redesigned to operate under positive pressure (rather than on suction), with resulting improved flame stability. The FPD was also equipped with a cooled photomultiplier and special optics to improve stability and enhance sensitivity.

Laboratory tests demonstrated the capability to monitor SO_2 at part-per-billion levels; however, the packaged instrument developed problems that resulted in reduced sensitivity. The demonstrated sensitivity showed an improvement over the previous instrument. Accurate calibration was not established due to both unresolved instability and limitations of the laboratory calibration system available. (While the tunability of the instrument suggests monitoring of other molecular species, only SO_2 was measured in this program.)

The final instrument permitted two modes of operation. In the sampling mode, approximately 700 liters per minute of sample was drawn through the instrument, of which approximately 0.4 liter per minute was burned for sulfur detection. In the calibration mode, the smaller flow could be introduced directly into the burner base.

SECTION 2

LABORATORY STUDIES

HELPAR UNIT REPAIR

The demonstration of the modified Helpar Unit at the Environmental Protection Agency, Research Triangle Park, North Carolina (EPA/RTP), at the end of the previous program was handicapped by several severe leaks that developed in the burner, possibly during shipping. The burner was carefully disassembled, at which time it was found that a leak approximately equal to sample flow was present. This leak was eliminated by capping the unused flame ionization detector with a Teflon cap. Automatic control of block and exhaust line temperature was also restored, thus bringing the instrument back to its original sensitivity and operation. This instrument has the monochromator and multialite as developed in the previous contract.

SAMPLE/HYDROGEN INTAKE SYSTEM

The intake system and burner were mounted in a large hood to allow quick design changes while working with sulfur dioxide (SO_2). For these studies, relatively high SO_2 concentrations were used to allow visual observation of emission characteristics with changes in parameters. SO_2 was leaked, drop by drop, through a silicone trap into the dilution system. Rate of SO_2 flow was estimated by counting drops.

The intake consisted of a Teflon-lined aluminum tube 3 inches in diameter and approximately 14 inches in length. A six-bladed muffin fan drove sample air through at approximately 30,000 cm^3/min. A 2-inch iris was used at the exhaust end to adjust back pressure and sample flow to the burner; however, it was later removed as unnecessary, burner intake being controlled by choice of inlet aperture.

The inlet to the burner was located approximately 11-1/4 inches from the fan, the burner being mounted on the intake tube. Details of the burner will be described later, but in essence, a small fraction of the total throughput

of the intake was sent through the burner as sample air, the amount being determined by a baffle just past the intake and the size and shape of the input channels.

In summary, the pressure intake is characterized by a large flow of sample air, of which a small part is used in the burner. There is probably little adsorption of sample on the fan blades or intake walls in this configuration, and there is much greater latitude in choice of actual air volume into the burner. The proximity of the burner inlet to the intake fan results in very rapid response to changes in SO_2 concentration.

BURNER DESIGN

First Burner Study

The first burner was modeled after the Meipar burner, but modified to fit onto the pressure intake system. The base of the burner consisted of a Teflon cylinder 2 inches in diameter and 2 inches high. The cylindrical burner head, containing the hydrogen and air inlets, was also made of Teflon. This head was threaded to fit into the burner base. Because of the difficulty of mating Teflon to Teflon, a flashback resulted on ignition, and the burner head was melted almost immediately.

A new burner head was milled from stainless steel, identical to the original Meipar head, but with a larger air inlet to allow sufficient flow with the pressure intake. The shield (and mixing chamber) of the original burner was omitted to allow experimentation with quartz tubes of various sizes. A hollow aluminum ring was press-fitted onto the stainless steel section to allow formation of a gas sheath around the flame. Thus the burner head had three concentric sections: a large central hole for the air sample, four symmetric hydrogen inlets very close to the central hole, and a ring of small holes for a sheath gas such as nitrogen. A pictorial representation of the burner is given in Figure 1.

First experiments were concerned with establishing a stable flame. The air and hydrogen flows were adjusted to approximately 200 cm^3/min as in the Meipar unit. Various short cylinders of quartz were now mounted on the burner head to replace the metal shield of the original Meipar. Stability was monitored by observing the 310-nm (OH) line, using the Farrand monochromator

and a 1P28 detector. The monochromator was positioned so that the centerline of the entrance slit lay about 12 mm above the burner head. Thus the monochromator viewed part of the flame itself (normally shielded in the Meiper) and some of the region above. Short bursts of SO_2 were admitted occasionally to allow visualization of the region of highest S_2^* emission.

In the first study, nine different quartz shields with outside diameters of 8, 9, and 10.4 mm, and heights of 6, 9, and 12 mm were placed on the burner head. It was observed that maximum flame stability was obtained for the 8-mm-diameter, 9-mm-height quartz shield. With the admission of SO_2, the blue emission was found to occur at the upper rim of the quartz shield. This flame was found to be extraordinarily stable, requiring deliberate smothering to extinguish. This is in contrast to the Meiper flame, which required accurate setting of gases and went out under small perturbations.

In another series of measurements, quartz tubes of 10.4-mm diameter and heights of 31 and 45 mm were used to determine the effect of greater shield lengths on the sulfur emission. First, the gas flows had to be adjusted to give optimum results. Sulfur emission occurred at the top of the 31-mm tube, but was within the 45-mm tube. While the longer tube contained the emission, it was found that the flame had lost its great stability.

Another series of measurements involved cooling with nitrogen. First, nitrogen was directed against the side of one of the shorter quartz shields to determine whether visual emission could be induced at a cold spot on the quartz. The results were negative. Nitrogen was then introduced through the aluminum annulus, using quartz shields in various positions. When there was an inner quartz shield (i. e., the nitrogen was cooling the shield from the outside) no increased emission was observed. When the inner quartz tube was removed so that the nitrogen formed a sheath about the hydrogen flame, increased emission was also not found. In the latter case, the cooling seemed to cause the flame to lift due to increased velocity of the gases. These negative results were surprising in view of other workers results; however, they are also tentative since the experiments were conducted with bursts of SO_2 and depended on visual observations.

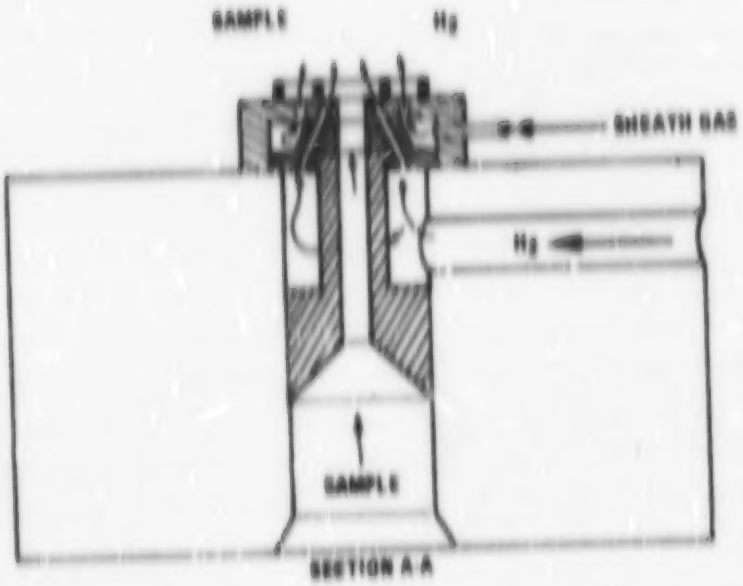

Figure 1. Modified burner head

The important conclusions we made from measurements on this first burner were as follows:

1. It was possible to obtain an extraordinarily stable flame using the pressure intake and a modified Meipar burner.
2. The region of maximum sulfur emission depended in detail on a large number of parameters that were not adequately controlled in the first burner.
3. Simple gas cooling methods did not produce an obvious visula increase in sulfur emission.

Second Burner Study

The first burner design was based on the Meipar unit with certain changes to accomodate a pressure system. The resulting burner demonstrated a greater stability than was possible with the Meipar vacuum unit. The second burner design is based in a general way on a burner design by Gilbert.[4] This design is characterized by a water-cooled chimney to enhance sulfur emission. Sample air is introduced around a central hydrogen jet, in contrast to the first burner. A schematic of the burner is given in Figure 2.

First measurements were made at relatively high SO_2 concentrations, usually exceeding 150 ppb, in order to allow visual estimation of emission geometry and intensity. Lower concentrations were detected with a monochromatorphotomultiplier combination. This latter system was set up so that the emitting region of the burner (see Figure 2) could be scanned spectrally or spatially. For spectral scans, the monochromator slit was oriented perpendicular to the axis of the burner to give best spatial resolution. For higher sensitivity measurement, the monochromator was rotated 90° to include as large a portion of the burner chimney as possible. Various spectral bandwidths from 2 to 20 nm could be chosen. The multiple slit developed in the first project was also available.

The first water-cooled jacket was approximately 15 cm long, with the burner chimney extending several centimeters out the end. The later, more compact version, approximately 10 cm long, resulted in no loss of emission

[4] Gilbert, P. T. Nonmetals. In: Analytical Flame Spectroscopy, R. Mavrodineanu, ed., New York, Springer-Verlag, 1970, p. 246.

efficiency and was therefore adopted for most measurements.

Cooling water temperature was varied from 30 to 70°C, with a broad optimum in the 40 to 50°C region. With our particular cooling bath, a minimum flow of 150 ml/min was necessary to prevent heating of the bath. A flow of 350 ml/min has been adopted as a nominal flow.

Total gas flow (air plus hydrogen) and the air/hydrogen ratio were varied independently. At high total gas flows, the emission extended higher up the chimney but with no evident increase in brightness. The actual flame region was longer, and emission from the (OH) line at 310 nm was scattered into the viewing region. At low total flows, the flame became unstable. Average requirements for the burner of Figure 2 were approximately 300 to 400 ml H_2 per minute and 250 to 275 ml sample per minute.

The burner was constructed to allow relatively easy replacement of the burner chimney. This allowed some variation in chimney geometry. The construction, evident in Figure 2, is an essential part of the design, affecting the cooling of the reactant flame gases. Using tubes of 7-mm I.D. and 8.5-mm O.D., various constrictions were fabricated. Chimneys with no constriction resulted in very weak emission. A constriction with an inside diameter of several millimeters seemed optimum. The position of the constriction relative to the end of the chimney also had an effect, a spacing of 15 mm being near optimum. A chimney with a 10-mm I.D. was constructed, but resulted in slightly decreased emission.

Spatial scans of the chimney above the constriction revealed that the sulfur emission remained essentially constant over the region between the metal end pieces of the water jacket. Spectral scans indicated that there was no discernible flame background in the sulfur region from 360 to 420 nm.

A simple opaque cylinder was fitted around the water-cooled region with a slit opening along one side. An aluminum reflector was placed opposite the slit to enhance emission through the slit. The monochromator was placed with its entrance slit about 24 mm from the axis of the chimney and parallel to the axis of the chimney. The monochromator was mounted on a double cross-feed, allowing vertical and horizontal positioning for optimization. The f/3.9 aperture of the monochromator was overfilled by the chimney emission, making distance from the axis uncritical.

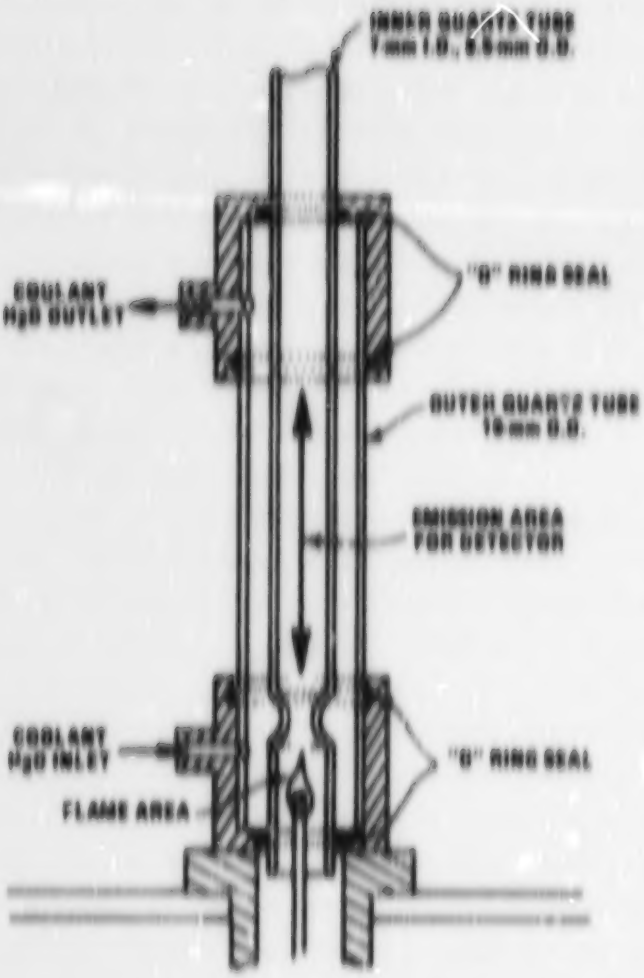

Figure 2. Cross section of upper burner region.

DILUTION CONTROL SYSTEM

Accurate calibration in the part-per-billion region is difficult. Our approach has been to use as simple a system as possible, producing stable samples in the concentration range of interest without demanding too great a degree of accuracy. Using a standard permeation tube with a measured output of 3.91 ug/min at 30°C, known SO_2 concentrations were produced using the dilution system shown in Figure 3. A flow of 10 liters/min over the permeation tube produced a concentration of approximately 110 ppb. Diluting 1 liter/min of this concentration with 10 liters of zero air produced a concentration of approximately 10 ppb. Alternately, diluting 0.1 liter/min of the original concentration with 10.9 liters/min of dry air produced a concentration of approximately 1 ppb.

Problems with this system included the following:

1. The lengthy tubing resulted in some SO_2 buildup in time, especially after use of high concentrations.
2. While the tubing was Teflon, several connectors were of glass or polypropylene, causing further buildup. More seriously, two inexpensive acrylic gauges were used in the sample line. This plastic is known to collect SO_2.
3. Because the controlled temperature bath was in use to supply water for chimney cooling, the permeation tube in its Teflon-lined outer tube was left at ambient temperatures in the hood. Turbulence in the hood could have been responsible for some of the long-time fluctuations observed.

ELECTRONICS

Final electronics for the prototype were to be constructed using those parts from the Helpar unit that were useful. For laboratory tests, a Keighley Model 416 High Speed Picoammeter was used for all measurements. Occasionally, the last stage of the Helpar modified electronics was used in conjunction with an x-y recorder to give 5-second time constants. (The Keithley is limited in this respect.) With enhanced flame stability, the photomultiplier noise becomes of some importance. After a demonstration showed the dramatic decrease in dark current possible, an EMR Low Noise

Tube Housing, Model 1150A, was purchased, along with an EMI 9781A. The dark current was approximately 6 x 10^{-11} amperes, after aging with high voltage in the dark.

COMPARISON WITH HELPAR UNIT

One goal of this project was to determine the improvement of signal/noise over the previous design. At the beginning of the present effort, the modified Helpar was repaired as discussed in section 2.1. Based on our measurements at RTP, we believe that the present modified Helpar, equipped with 2-mm entrance slits and 3.5-mm multiple exit slits, was slightly more sensitive than a standard Helpar unit. We therefore compared the new burner with the modified Helpar. The same slits and electronics were used in each case, except for the photomultiplier. The Helpar unit was operated in parallel with the new burner, sampling excess gas from the last mixing stage.

Figure 4 and 5 show laboratory data on a series of measurements taken alternately on our second burner and the modified Helpar. The time scale, from right to left, was one-half minute per major division. The detector was an EMI 9781A in the SSR 1150A low noise housing. High voltage was 750 volts, supplied by a Baird 312A. The output of the Keithley 416 was coupled into the last two stages of the Helpar revised electronics to allow a 5-second time constant on the recorder.

In Figure 4, we show the response of the current burner at a nominal concentration of 10 ppb, using the 0.1 x 10^{-9} ampere scale on the electrometer. The average signal was quite constant over the 6-1/2-minute period, the peak noise amounting to approximately 10 percent of the average. The signal from the dilution air (hopefully SO_2-free) is indicated in the second section of this trace. Its amplitude was less than 10 percent of that of the 10 ppb sulfur, except for a rise in the last 2 minutes.

In the modified Helpar unit on the same current scale, the sulfur signal was indistinguishable from background, despite the fact that the phototube in the Helpar (EMI 9526B) has a gain about ten times greater than the EMI 9781A used with the new burner. Increasing the gain to the 0.1 x 10^{-10} ampere scale (a current gain of thirty), we see in Figure 5 the results for the same 10 ppb SO_2 measured by the Helpar. The signal from dilution air (not shown) was approximately zero on the chart. The signal

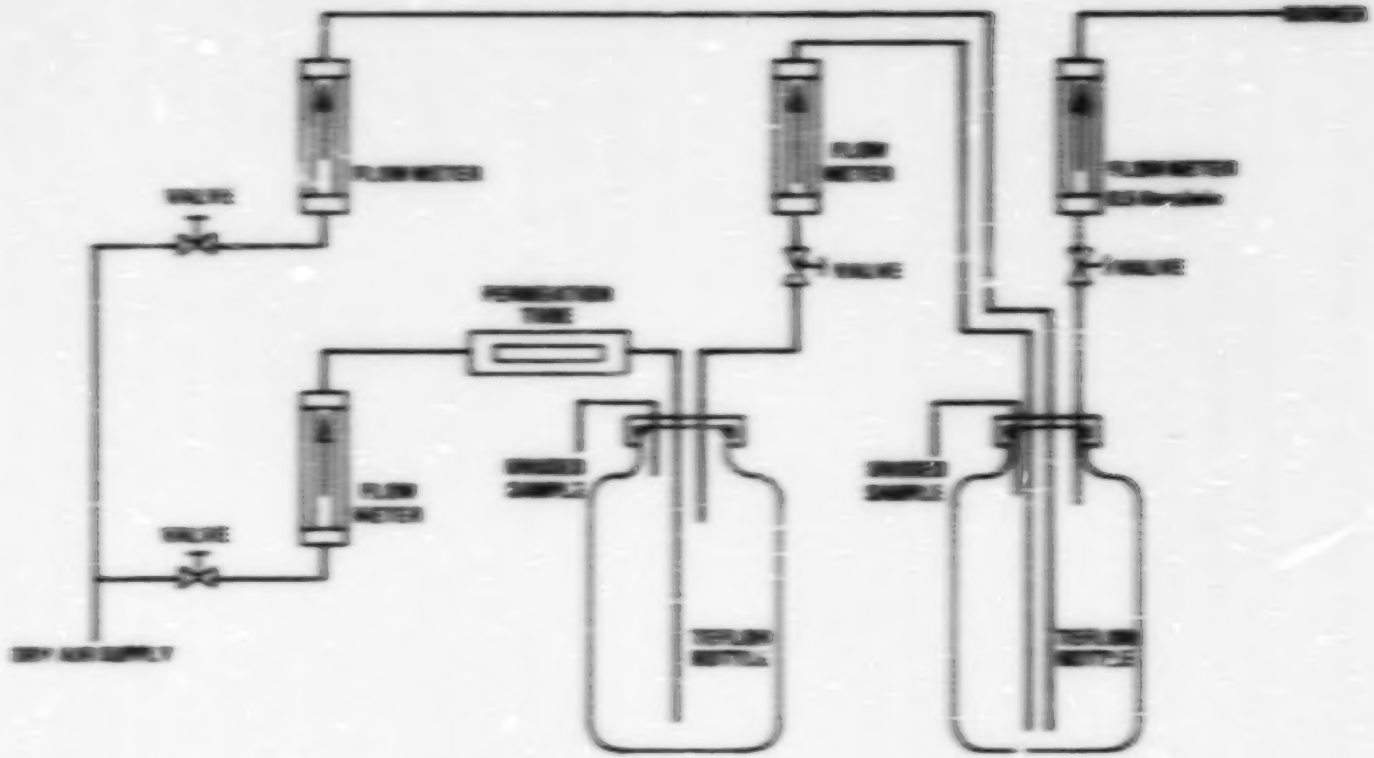

Figure 2. [illegible]

from the SO_2 was characterised by a general upward drift over the 24 minutes of observation. Superposed were broad oscillations with a period of approximately 5 minutes. The amplitude of the oscillations was near 50 percent of the average signal.

It should be noted that apparent rapid response between zero gas and sample was not real; the recorder was shut off during switching and some time given to establish equilibrium. In practice, we noted a relatively rapid buildup when increasing concentration, but a much slower decrease on reducing concentration. We feel that this was due to accumulation in rather long mixing and sample lines. That the lines did clear out is indicated in the low response of the dilution air used after sufficient time.

In contrasting the sulfur signals from Figures 4 and 5, it is clear that the sensitivity of the new burner was much greater than the older Meipar, yielding a relatively steady output, whereas the Meipar output was hardly usable at this gain level.

MEASUREMENTS AT 1 ppb

An important goal of this project was to demonstrate usable sensitivity at levels under 1 ppb. In order to test this, we endeavored to produce approximately full-scale chart deflection at this concentration, with usable signal-to-noise ratio. Data for such a measurement are contained in Figure 6. Figure 6b is a continuation of Figure 6a. The setup was similar to the previous measurement, except that the current scale was 1×10^{-9} amperes. Note the dramatic improvement over the 10-ppb measurement of Figure 4.

FINAL MODIFICATIONS

Following the measurements at 1 ppb discussed in the previous section, numerous refinements were made, including modification of the burner base to allow better mixing in the "calibrate" mode. The instrument was then assembled in the housing with covers for final tests. The exhaust was redirected into the sample flow to minimise water buildup. A final calibration was next attempted.

The calibration was unsuccessful due to unexpected drift in the baseline signal. This was attributed to temperature fluctuations in the housing, giving rise to drift in photomultiplier dark-current. While a fan helped

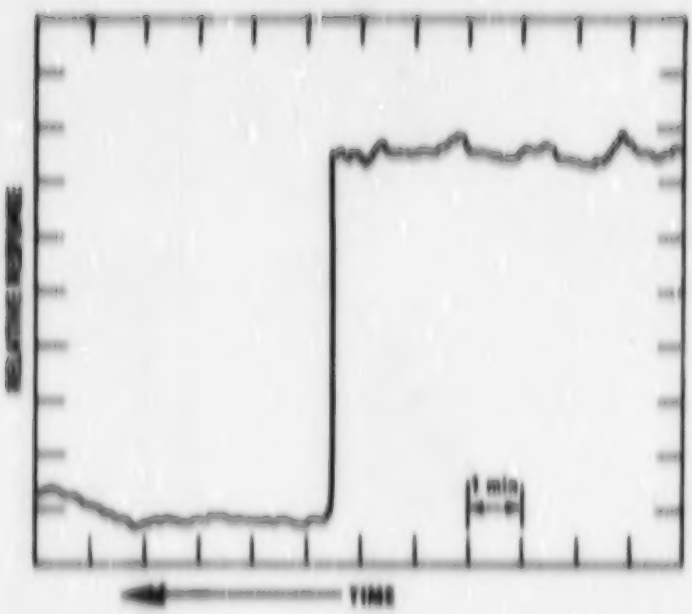

Figure 4. Response of second burner to 10 ppb SO_2 and dilution air (0.3×10^{-9} ampere scale).

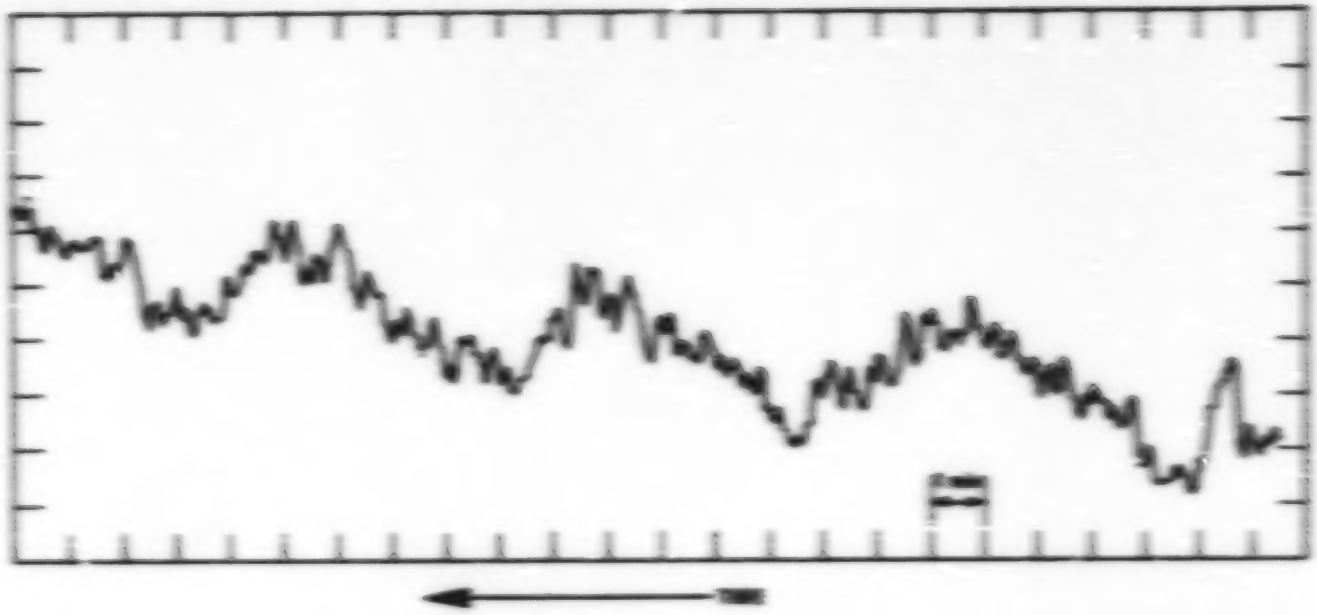

Figure 5. [illegible]

to reduce the drift, it was still too large to permit reproducible measurements in the 1-ppb region. Rather than ship the instrument in this condition, additional modifications were proposed, which we felt would correct the problems. The most important suggestion was to stabilize the temperature of the photomultiplier through use of a thermostatted housing.

The original photomultiplier (EMI 9781A) was mounted inside the instrument with not enough clearance to permit installation of an insulated housing. Therefore it was recommended that the photomultiplier be mounted directly above the multiple exit slits of the polychromator, necessitating projection through the top cover. Since this new geometry demanded new optical coupling, it was recommended that further improvement be achieved by use of a new selected low-noise photomultiplier in a thermostatted housing. This would not only reduce temperature drifts, but would also further increase signal/noise, thus enhancing useful sensitivity. The recommended replacement photomultiplier was an EMI 9789QA, mounted in an RFI/2010 cooler. This photomultiplier is unusual in that it has a very small (10 mm) photocathode and correspondingly low dark current. It was proposed that the "frost-free" window in the housing incorporate quartz lenses to image the multiple exit slits on the photocathode. An optical schematic of the new detection system is given in Figure 7.

Recommendations incorporating these suggestions, together with request for further funding to allow installation and test, were made in July 1973. There followed lengthy consultations and negotiations, during which time the instrument was placed in storage. Finally, negotiations that stipulated that the government would furnish the suggested cooled detector system were completed. The latter was received, with special frost-free window, in June 1974.

It had been hoped that installation of the new detector system would be straightforward and that immediate improvement in instrument sensitivity would be realized. Following final calibration, the instrument would be tested and demonstrated at RTP. Unfortunately, this was not to be the case. For reasons not understood by us, a decrease in sensitivity was observed. Since time and funding did not permit a thorough recheck of all portions of the instrument to locate the problem(s), the final instrument was shipped and demonstrated at RTP in July 1975.

Figure 6. [illegible]

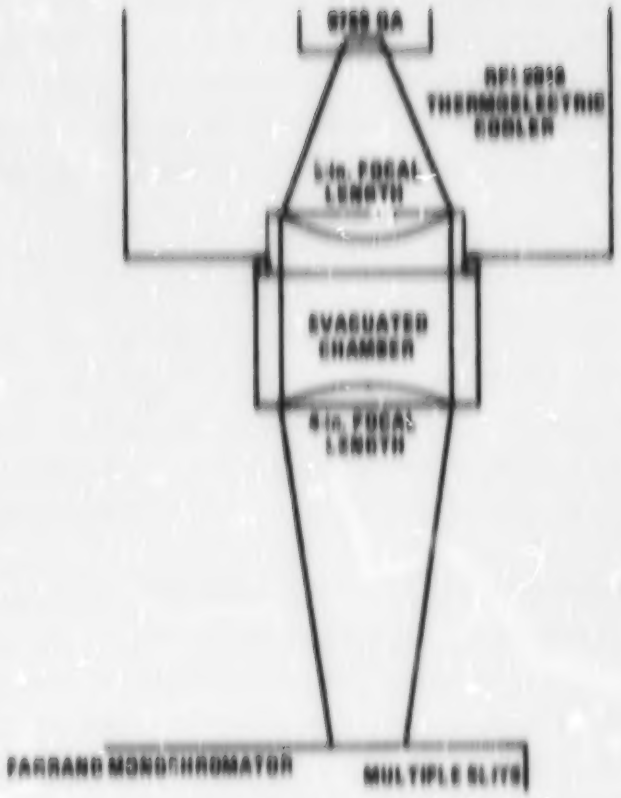

Figure 7. Optical schematic of new detection system (approximately to scale).

A great deal of effort was expended, in the brief time available, to locate the source of the problem. It was found that it was best to reduce the high voltage on the new photomultiplier to 1100 volts, since spurious noise spikes appeared at higher voltages. It was also observed that no measureable improvement was noted when the photomultiplier was cooled to -20°C. Therefore a setting close to 0°C was adopted. The temperature of the cooling water for the quartz chimney was varied from ambient to 70°C, with the higher temperatures being only slightly better. The burner was disassembled and cleaned repeatedly, with no improvement. The polychromator was checked, and all optics found clean. In short, the sensitivity reported in the previous section was never regained. Nevertheless, even the reduced performance was believed to be a significant improvement over the earlier design.

FINAL CALIBRATION

On 27 June 1975, Dr. R. K. Stevens of EPA/RTP visited the Baird-Atomic laboratory to observe the instrument and arrange for delivery to RTP. It was agreed that the instrument would be calibrated for a most sensitive scale of 10 ppb or less. Final calibration was carried out by Dr. L. Dieting. (L. Campbell, who had done much of the earlier work, had left for other employment.)

Final calibration was hampered by an imprecise source of calibrated SO_2, an unknown (and possibly varying) background of SO_2 in the mixing air, and some erratic behavior of the instrument. Nevertheless, over a period of several days just prior to shipping the instrument for demonstration to RTP, data were taken at nominal concentrations ranging from approximately 6 to 18 ppb. (Data at higher concentrations were also taken but were discarded due to an obvious breakdown in the SO_2 calibration system.) While these data are felt to be of limited accuracy and cover only a restricted concentration range, they provide information on the final sensitivity of the instrument and the nature of the dependence of SO_2 concentration. The data are plotted in Figure 8.

Theory predicts a response that depends on the square of the concentration of total SO_2. If the mixing air for preparing known SO_2 concentrations with a permeation tube also contains a measureable background of SO_2 (or other

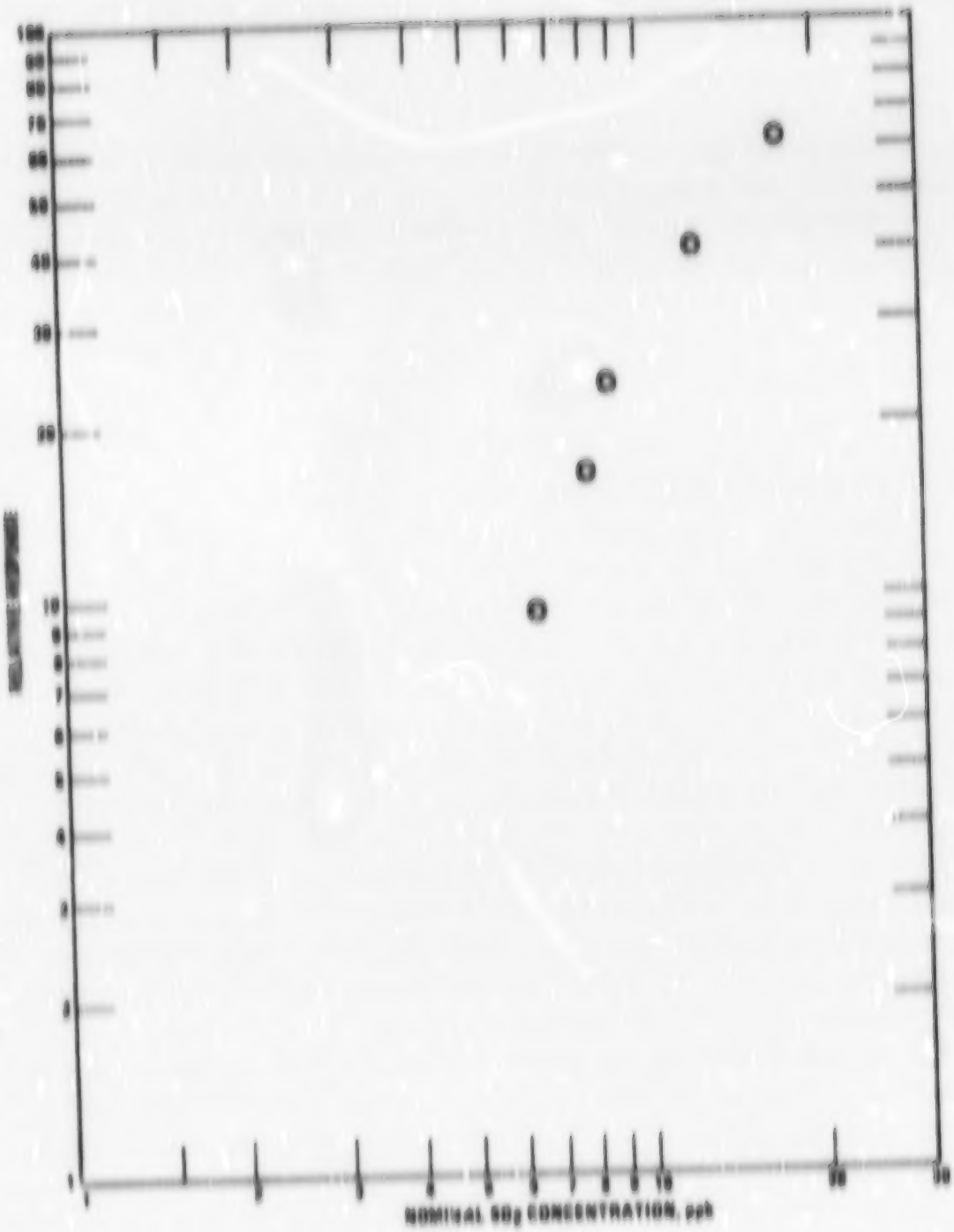

Figure 8. Final calibration.

sulfur-containing molecule), then the apparent response to calibrated SO_2 departs from quadratic at concentrations approaching that in the mixing air; at concentrations much less than in the mixing air, the dependence should be linear.

The limited data of Figure 8 do not allow too much analysis; however, several conclusions may be drawn. The apparent slope lies between 1.5 and 1.8. The two data points for the lowest concentrations indicate an increasing slope at lower concentrations. This is probably not true, but reflects the problems with the calibration technique. The response for the data point was 38 percent of full scale on the 10^{-8} amp range. Assuming a quadratic dependence, this would predict a full scale reading of just over 3 ppb on the 10^{-9} amp scale.

DEMONSTRATION AT RESEARCH TRIANGLE PARK

The instrument was installed and demonstrated at EPA/RTP on 24 and 25 July 1973 by Drs. A. Hornig and L. Giering. While the instrument survived shipment very well, other problems arose at the laboratory. The calibrated SO_2 system available was not able to deliver the required 0.5 liter/min at a pressure sufficient to allow proper use of the calibration mode. There was, of course, no calibrated SO_2 source capable of delivering approximately 700 liters/min for the ambient sampling mode. Therefore, the only measurements possible that satisfied the design inputs involved measurement of ambient laboratory air.

After uncrating and assembling the instrument, first measurements were made in comparison with a Meipar unit on ambient laboratory air. Figure 9 contains a tracing made from data taken during this test. Note that the instrument "zero" is obtained by detuning the monochromator to approximately 200 nm, well out of the sulfur emission region.

The Meipar unit made use of prototype "zero air" generator, under test at RTP. This allowed selection of known concentrations from "zero air" to many parts per billion SO_2. While response to known sulfur concentrations seemed reasonable, when ambient laboratory air was monitored the reading was less than that for "zero air", as indicated in Figure 10. This anomalous result could not be explained; however, the Meipar unit could not detect the

sulfur background present in the laboratory. It should also be noted that there is a periodic fluctuation in the signal.

The second day was spent trying to calibrate our instrument using the calibrated supply. The "zero air" generator did not operate properly when attached to the Baird prototype, overheating many times and melting connectors. In comparison with the Helper unit, the Baird instrument displayed poorer signal/noise, along with unexplained periodic changes in sensitivity. It is unclear what part of this was due to makeshift sampling arrangements. Some of the sensitivity variation seemed related to accumulation of water in the burner.

Figure 9. Response of Baird instrument to SO2 in ambient laboratory air at RTP.

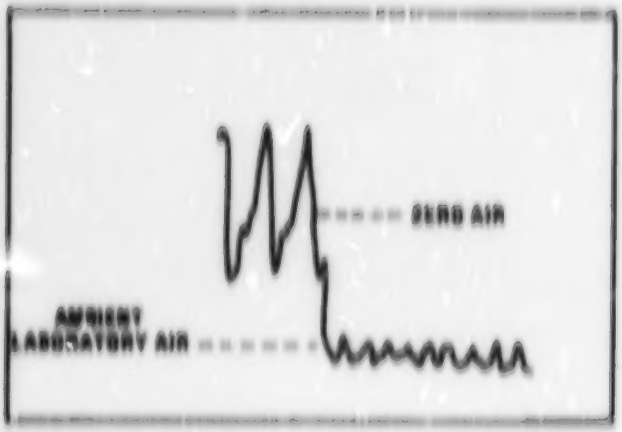

Figure 10. Response of Meiner instrument to SO2 in ambient laboratory air at RTP.

SECTION 5

CONCLUSIONS

This program has produced a novel instrument that differs in several important ways from its predecessors. First, the instrument employs a polychromator with correlation mask to detect only major S_2 emission lines, resulting in high specificity for sulfur compounds. An oscillating mechanism allows further enhanced specificity in the difference mode by comparing peaks and valleys of the emission spectrum. While the instrument was demonstrated only for sulfur, its tunability permits extension to measurement of phosphorous, arsenic, and selenium compounds, and perhaps others. The redesigned burner operates under pressure, sampling only a small fraction of the sample volume. This results in an exceedingly stable flame, rapid response to changes in concentration, and small sample buildup. The cooled flame, viewed at some distance from the actual hydrogen flame, results in high sensitivity for sulfur and low flame background.

Several unsolved problems remain. The SO_2 calibration system was inadequate to produce reproducible standard concentrations in the 1-ppb range. Proper calibration at this level will require much greater sophistication. There remains the unsolved problem of deterioration of sensitivity after the year's storage and reactivation of the instrument. Because the calibration mode was added after design of the primary sampling mode, the present instrument does not allow easy interchange between the two and requires awkward use of gauges. The difference mode has not been optimized and has electronic and mechanical problems. The sample flow rate of 700 liters/min is overly large and could be substantially reduced, using a smaller manifold and fan.

SECTION 4

RECOMMENDATIONS

In light of the unexplained deterioration in performance of the instrument as delivered, it is first recommended that the entire instrument be rebuilt, correcting the problems listed in the previous section, and making it easier to operate in both calibrate and sampling modes. Prior to final redesign, several methods of enhancing sensitivity should be explored, including auxilliary optical excitation and use of selective surface sensitizers to increase sulfur emission. Finally, the use of the instrument for other molecular species should be explored.

APPENDIX A

INSTRUMENT DESCRIPTION AND OPERATION

DESCRIPTION OF THE INSTRUMENT

The instrument consists of a main housing with several accessories. The main unit houses the sample intake, the burner, detector system and necessary electronics to analyse for sulfur dioxide. A fan in the main housing pulls a large volume of sample (.700 liters/min) through a 1-inch duct. A small fraction of this (0.3 to 0.4 liters/min) is introduced into an enclosed burner together with hydrogen from an auxiliary tank. Hydrogen flow is set by a valve and gauge in the front panel to approximately 200 ml/min. In the resulting hydrogen-rich flame, sulfur dioxide is reduced to form excited molecular sulfur, S_2^*. The deep blue chemiluminescence is observed above the visible portion of the flame in a water-cooled quartz column. A polychromator with multiple exit slits matching S_2 band structure sums this emission, which is amplified by a standard photometer. The excess hydrogen and moisture is redirected into the main sample exhaust. The burner also has a calibration mode allowing direct introduction of known SO_2 concentrations.

There are two basic modes of operation. Highest sensitivity is obtained in the normal mode when the polychromator is tuned to the multiple line emission of S_2^*. In the difference mode an internal motor tunes the polychromator alternately to the peaks and valleys of the S_2^* emission spectrum, the output being the difference between peak and valley readings. This mode achieves higher selectivity at the cost of sensitivity. The overall signal level decreases by about a factor of two.

The photometer consists of a Heiper amplifier and high voltage supply modified to permit difference measurements. A cooled photomultiplier, added in the last phase of this project, protrudes above the main housing. Outputs of 1 millivolt or 1 volt full scale are available for display on a strip chart recorder (not supplied).

External cooling water is required for both the thermoelectric cooler and the quartz column. For best results, a cooling bath should be used to maintain the quartz column at 50°C. The controller for the cooled photomultiplier tube is in a separate housing. Variation in photomultiplier temperature from -20° to 10°C showed little influence in signal/noise ratio; the more important function of the cooler is to maintain the photomultiplier at a constant temperature.

SAMPLE/HYDROGEN SYSTEM

Ambient Airflow System

An ambient air sample is supplied by a Cyclonair Blower, CNE 1, Metron, Inc., Woodstock, New York. The air intake is approximately 700 liters/min. A small fraction (0.3 to 0.4 liters/min) of this large air intake, which is directed at the base of the burner, is sampled through slotted holes in the base of the burner. The flow to the burner is regulated in the sample mixing chamber by opening or closing these holes with the flow valve. A more complete description of the burner can be found in A.3.

Calibrated Airflow System

A calibrated SO_2 sample can be introduced into the burner by attaching the Teflon line in the rear of the instrument to a system that supplies the desired concentration of SO_2 at a flow of 0.350 to 0.375 liters/min.

Sample Flow Control

A lever on the burner assembly allows switching from the calibrated to the ambient air sample mode. As the lever is moved from position C (calibration) to position A (ambient), the flow valve moves so as to close the calibration air inlet and open the ambient air inlet. Small variations about position A serve to regulate the airflow in the ambient mode.

Hydrogen Gas Flow

The hydrogen for the burner is supplied through a rotameter in the instrument to the base of the burner where it is mixed with air. The flow of hydrogen should be 0.425 to 0.475 liters/min. The calibration curve for the rotameter is given in Figure A.1.

THE BURNER

The burner assembly (see section A.9, drawing number 5409-1000) attaches to the blower and sits in the main stream of the ambient air intake. The bottom base of the burner is a cone-shaped piece with four slots (90° apart) to allow a small fraction of the large volumn of intake air to enter the burner. The cone shaped burner base also has four holes (90° apart), set in a circle concentric with a circle through the centers of the four slots, approximately 1/2 inch from the edge of the burner base. These four holes allow only calibration samples to enter the burner and are not connected to the ambient air source. The hydrogen enters the burner through a stainless steel nozzle that fits into the center of the piece cut with four holes and four slots. Hydrogen is not premixed with the sulfur dioxide sample. A Teflon seal fits on top of the burner base with a series of holes and slots cut out to match the burner base top. A stainless steel plate with four holes acts as a flow valve as it either partially or fully opens or closes the four slots or four holes. A mixing chamber and the base section of the burner sit on top of the cone-shaped burner base. The hydrogen nozzle is held in place by a spring washer and retainer nut. In assembling the burner, it is important to make sure the tip of the nozzle is aligned with the line scribed on the inside of the inside of the burner. An o-ring and two Teflon plugs seal and secure the burner to the quartz chimney. A wire passing through one of the Teflon plugs is used for flame ignition.

The cooled quartz column is designed with a constriction to cool and enhance the emission of the reactant flame gases. The constriction is located approximately 15 mm from the end of the chimney. The design of the upper burner region including the quartz column is shown in Figure 2.

A rectangular block equipped with a water inlet and outlet serves as a cooling jacket for the quartz column. A viewing window cut out of the cooling jacket is mounted directly to the entrance slit of the monochromator. In order to remove the water fromed in the reaction with sulfur dioxide and hydrogen, a tube is attached to the exhaust end of the quartz chimney. The tube is directed into the 1-inch duct near its exit, creating a slight vacuum to air in the removal of water.

DETECTION SYSTEM

A modified Farrand Monochromator with a single 5-mm entrance slit and a five-slit exit mask is used. A Gencon cooled photomultiplier tube housing equipped with an EMI 9789 QA tube is used for detection. The "frost-free" window in the housing incorporates quartz lenses that focus a reduced image of the exit slits into the small (10-mm) photocathode.

ELECTRONICS

Final electronics for the prototype were constructed from various Heiper parts. The amplifier is mounted in a shielded sub-assembly with three access holes to adjust amplifier offset and gain. The gain settings on the front panel apply to the internal calibration of the amplifier and to all amplifier settings, except for the log-linear scale, which has been disconnected. The original two-position time constant toggle switch has been replaced with a four-position switch. The first three positions allow time constant selection of 0.1, 1.0, and 10.0 seconds. The fourth position is open for an additional time constant selection (utilizing an external capacitor).

In the <u>differential mode</u>, the S_2 peaks and valleys are imaged alternatively on the multislit mask. In this mode, background is automatically subtracted and specificity is improved. To accomplish this, a 4-mm-thick quartz plate is mounted in the exit beam of the monochromator, just before the multislit. The monochromator is tuned so that the five strongest S_2 lines are registered on the multislit mask when the quartz plate is oriented perpendicular to the beam. As the plate is rotated in the beam, the sulfur lines are displaced until they are not transmitted by the multislit mask.

FRONT PANEL INDICATORS AND CONTROLS

A brief description of the front panel indicators and controls is given below.

<u>Panel Labels</u>	<u>Function</u>
HYDROGEN	Adjusts the flow of hydrogen gas to the burner.
POWER	Delivers 110 V a.c. to the instrument via a three position switch Center - Apparatus off Down - Electronic component warmup Up - Operation

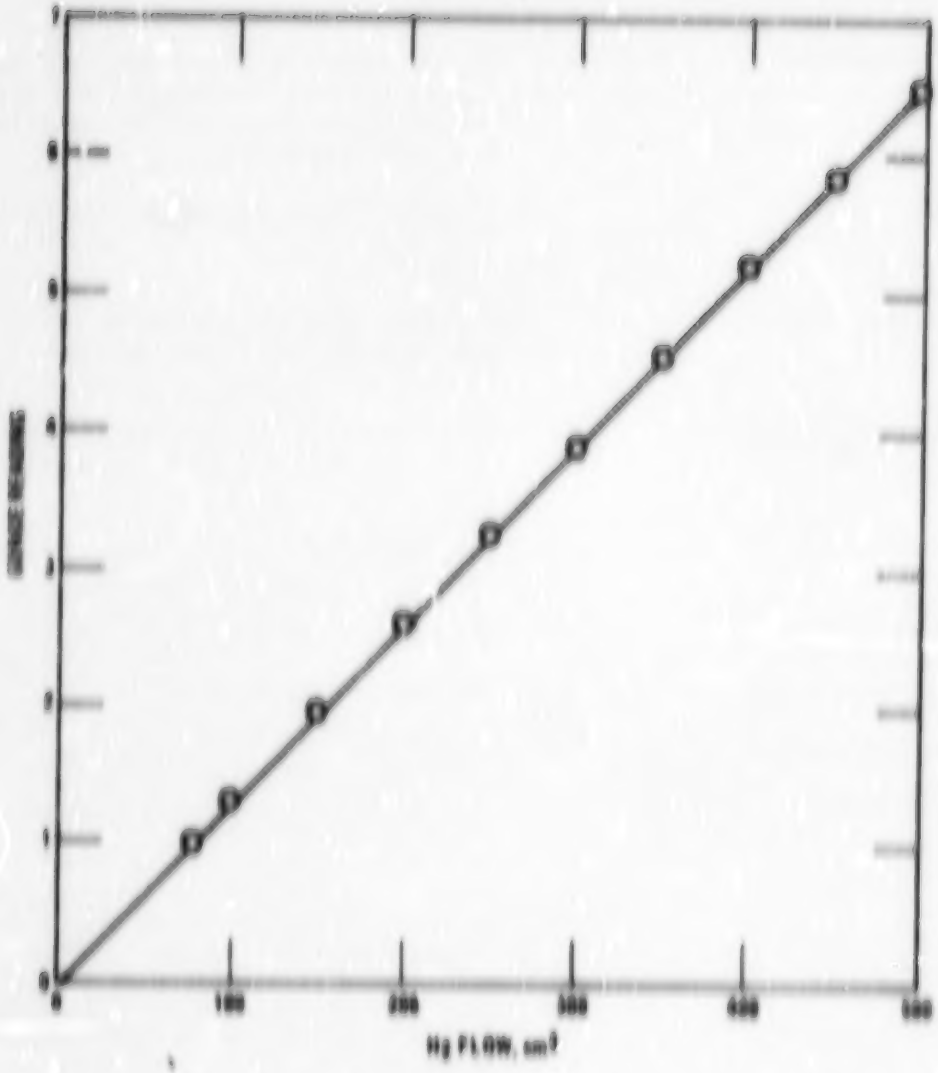

Figure A-1. Calibration of hydrogen rotameter.

Panel labels	Function
IGNITION	Ignites the hydrogen-air mixture by a high voltage discharge.
OFFSET	Provides up to 5 x 10^{-8} amps buckout current.
TIME CONSTANT	Allows selection of 0.5 sec, 1.0 sec, and 10 sec time constants. Two spare positions are available for additional external capacitors.
RANGE AMPS	Provides linear current amplification ranges for 10^{-13} to 10^{-4} amps full scale.
CALIBRATE AMPS	Provides internal signals to allow periodic calibration of the photometer.
CHOPPER	Actuates oscillatory quartz plate mechanism to allow difference measurements.
OUTPUT	Provides 1 mV and 1 V full scale signals for an external recorder.
FLAME	(No longer used.)
CALIBRATION AIR	(No longer used.)
INTERIOR ADJUSTMENTS	
MONOCHROMATOR	The modified Farrand monochromator has been adjusted so that the five principal S_2 emission lines fall on the multiple exit slit. Readjustment is possible by maximizing signal while retuning the monochromator. Using a combination of the large coarse tuning dial and the center fine tuning screw. This adjustment must be made with the cover off.
CHOPPER ASSEMBLY	In order to disengage the differential mode completely, the chopper drive must be in the maximum upward position. This adjustment must be made with the top cover off.

Panel labels	Function
SAMPLE CONTROL	A lever on the burner assembly allows switching from ambient air (position A) to calibration air (position C).

OPERATING PROCEDURES

Setup

Prior to start of air monitoring, the following should be done:

1. Connect hydrogen supply line to inlet on left side of panel.
2. Connect water lines from a constant temperature bath to the burner chimney. Set water temperature at approximately 30°C.
3. Connect high voltage input and signal output cables from the photomultiplier to the electronics module.
4. Connect cooling water fro thermoelectric cooler to photomultiplier housing.
5. Connect the instrument to a 110-volt power source.
6. Set the range selector switch to the appropriate linear (amplification scale. For ambient air, this is 10^{-8} amps. The calibrate switch should be in the normal position and the time constant/switch set at 1 sec.
7. For calibration air, the sample line must be connected to the back panel and the lever on top of the burner must be in position C.

Startup

Warmup--

1. Turn instrument power switch to "down" position to allow the electronic components of the system to stabilize.
2. Dark current check: Turn range switch to 10^{-6} amps and time constant switch to ½ sec. Adjust operational amplifier offset to read zero on recorder or voltmeter. Turn gain switch to 10^{-11} amps and time constant switch to 10 sec and adjust dark current to zero. Recheck "0" setting in 10^{-6} position.

Water Cooling--

Turn on water to cooling jacket for thermoelectric cooler then turn on thermoelectric cooler. (Initially, the current reading should be 7 to 8 amps; at a reading of 1 amp, the tube has reached thermal stability.) Turn on chimney cooling water.

Ignition--

1. Turn main power switch to "up" position. (Blower can extinguish flame if started after ignition.)

2. Ambient mode: With hydrogen off, adjust airflow to 0.375 to 0.400 liter/min by moving the lever on top of the burner. Turn on hydrogen supply with needle valve closed. Slowly open needle valve and press ignition switch. Ignition is confirmed by a persistant meter reading above the dark current. Adjust hydrogen flow to 0.425 liter/min.

3. Calibration mode: Switch burner valve to calibrate position (position C). Disconnect glass tube from end of burner exhaust to main exhaust manifold. Check for zero flow through burner by inserting flow gauge (Lab Crest flow meter #448-118). Open calibration air supply and adjust air flow to 0.375 to 0.45 liter/min. Ignition procedure is the same as the ambient mode. Adjust hydrogen flow to 0.425 liter/min. Ignition is confirmed by a persistant meter reading above dark current.

Turnoff

1. Turn off hydrogen supply.

2. Turn off calibration air, or blower if monitoring ambient air.

3. Turn off SO_2 monitor power switch.

4. Turn off all cooling water.

Miscellaneous

1. Airflow in excess of 0.500 liter/min produces high temperature capable of fracturing the quartz burner.

2. Maximum measurable flow of hydrogen is 0.500 liter/min (6.5 on the flow gauge).

3. Large injection of SO_2 will result in build up of SO_2 in the calibration lines.

SCHEMATICS

Table A-1 indexes the fifteen mechanical and one electrical schematics. The schematics are tabulated by drawing number and title.

TABLE A-1. INDEX OF SCHEMATICS

Drawing number	Title
5409-0100	Right side--Low-level SO_2 monitor
5409-0101	Front panel--Low-level SO_2 monitor
5409-0102	Prototype--Low-level SO_2 monitor
5409-1000	Burner Assembly
5409-1001	Burner Cooler Assembly

TABLE A-1. INDEX OF SCHEMATICS

Drawing number	Title
5409-1002	Burner Cooler
5409-1003	Cap, Burner Cooler
5409-1004	Mixing Chamber
5409-1005	Flow Valve
5409-1006	Retainer Nut
5409-1007	H_2 Nozzel
5409-1008	Burner Base
5409-1009	Burner Support Bracket
5409-1010	Flow Valve Adjustments--Parts and Assembly
5409-1011	Sample Manifold
5409-1012 (a)	SO_2 Monitor Wiring Diagram